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NATO-ADVANCED STUDY INSTITUTE

STRUCTURE-PROPERTY RELATIONSHIPS IN ION-BEAM SURFACE-MODIFIED CERAMICS--THEORY AND APPLICATIONS

IL CIOCCO, CASTELVECCHIO PASCOLI, ITALY

August 28 - September 9, 1988

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F. A. Smidt	Naval Research Laboratory, USA
A. Anttila	University of Helsinki, Finland
M. Nastasi	Los Alamos National Laboratory, USA

GENERAL INFORMATION

MONEY MATTERS

Hotel Accounts

An account will be opened for each person attending. Please be sure to check out at the desk even if the organizers are paying for your room and board in order that the computer will get the message that you are gone. If you are on a scholarship, the organizers will pay for room and board directly to the hotel. You pay hotel for any extras. Everyone else should deal directly with the hotel.

Tips

The hotel management suggests a small tip of about $10 per person for the full period would be appreciated by the staff. If you wish to contribute, place the money in an envelop and turn in to the conference desk. The hotel manager will distribute to the staff.

Other

The hotel will accept all major credit cards and Eurochecks. It will cash Travelers Checks and convert major currencies, imposing a small commission. Please contact the hotel desk for service.

TRANSPORTATION

We will provide two buses to Pisa on Saturday, September 10. If you wish to use this service, please sign up at the conference desk indicating the time and means of departure from Pisa.

MANUSCRIPTS

Please turn in at the conference desk as soon as possible. We will conduct the reviews during the term of the Institute. We will make minor corrections at Oak Ridge. The organizers hope to leave Il Ciocco with all manuscripts having been reviewed and with the author's corrections. Publication is promised within four months after the publisher receives the package of manuscripts from the organizers.

PROCEEDINGS

Each registrant will receive one copy of the proceeding free.

PROGRAM

Sunday, August 28, 1988

1500 - 1900	Registration
1900 - 2030	Welcome Drink
2030	Dinner

Monday, August 29

CHAIRMAN: W. O. HOFER

0830 - 0900	Opening of Institute
0900 - 1000	C. R. A. Catlow, University of Keele, UK "Calculation of Defect Properties of Ceramics"
1000 - 1030	Break
1030 - 1130	Catlow Continued--
1130 - 1200	Discussion
1200 - 1230	I. Singer, Naval Research Laboratory, USA "Ion Beam Alloying of Ceramics at High Temperatures"
1245	Lunch
1700 - 1730	Coffee/Juice
1730 - 1930	P. Mazzoldi, University of Padova, Italy "Disorder, Randomness, and Amorphous Phases"
1930 - 2000	Discussion
2015	Dinner
2130	Introduction to Tuscany Wines and Cheeses of the Region

Tuesday, August 30

CHAIRMAN: W. O. HOFER

0830 - 0930	D. M. Parkin, Los Alamos National Laboratory, USA "The General Displacement Cascade in Solids"
0930 - 1000	Break
1000 - 1100	Parkin Continued--
1100 - 1130	Discussion
1130 - 1200	J. T. A. Pollock, CSIRO, Australia "Enhanced Hardness and Wear Resistance in Polymeric Carbons by Ion Implantation"
1200 - 1230	B. D. Sawicka, Chalk River Laboratories, Canada "Properties of Iron-Implanted Diamond"
1245	Lunch
1700 - 1730	Coffee/Juice
1730 - 1930	J. Schou, RISO National Laboratory, Denmark "Ion Energy Dissipation and Sputtering During Bombardment of Multicomponent Materials"
1930 - 2000	Discussion
2015	Dinner

PROGRAM (continued)--

Wednesday, August 31

CHAIRMAN: T. F. PAGE

0830 - 0930	F. W. Saris, FOM, The Netherlands "Mechanisms of Ion Beam Mixing"
0930 - 1000	Break
1000 - 1100	Saris Continued--
1100 - 1120	Discussion
1120 - 1150	G. Battaglin, University of Padova, Italy "Ion Beam Mixing of Fe in SiO_2"
1150 - 1220	K. Padmanabham, Wayne State University, USA "Dynamic Ion Implantation in Thin Ceramic Films"
1230	Lunch
1330	Excursion to Pisa
2030	Dinner

Thursday, September 1

CHAIRMAN: T. F. PAGE

0830 - 0930	P. Thevenard, University Claude Bernard, France "Defect Creation in Ion Bombarded Inorganic Insulators"
0930 - 1000	Break
1000 - 1100	Thevenard Continued--
1100 - 1130	Discussion
1130 - 1200	J. A. Sawicki, Chalk River Laboratories, Canada "Structural Properties of Iron-Implanted ZrO_2"
1200 - 1230	E. Abonneau, University Claude Bernard, France "Microstructural Characterization of Ion Beam Mixed Al_2O_3/Cu Interfaces"
1245	Lunch
1700 - 1730	Coffee/Juice
1730 - 1930	J. L. Whitton, Queen's University, Canada "Ion Beam-Induced Crystalline to Amorphous Transformations in Ceramic Materials"
1930 - 2000	Discussion
2015	Dinner

PROGRAM (continued)--

Friday, September 2

CHAIRMAN: J. M. RIGSBEE

0830 - 0930	R. Kelly, IBM, USA "Compound Formation and Chemical Factors in Ion Beam and Laser Treatments"
0930 - 1000	Break
1000 - 1100	C. J. McHargue, Oak Ridge National Laboratory, USA "Ion Beam Mixing of Metals and Ceramics--Material Considerations"
1100 - 1130	Discussion
1130 - 1200	B. Van Hassel, University of Twente, Netherlands "Ion Implantation in Zirconia"
1200 - 1230	L. Romana, University Claude Bernard, France "Ion Beam Mixing and Annealing of Metal/Sapphire Structures"
1245	Lunch
1700 - 1730	Coffee/Juice
1730 - 1930	T. F. Page, University of Newcastle upon Tyne, UK "Changing the Mechanical Properties of Ceramics by Implantation"
1930 - 2000	Discussion
2015	Dinner

Saturday, September 3

Excursion to Florence
Late dinner

Sunday, September 4

Excursion to Sienna/San Gimignano
Late dinner

Monday, September 5

CHAIRMAN: J. M. RIGSBEE

0830 - 0930	R. Kossowsky, Pennsylvania State University, USA "Tribological Properties of Ion Beam Modified Ceramics at Elevated Temperatures"
0930 - 1000	Break
1000 - 1100	Kossowsky Continued--
1100 - 1130	Discussion
1130 - 1200	D. L. Joslin, University of Tennessee, USA "Thin Film and Near-Surface Characterization Using a Mechanical Properties Microprobe"
1200 - 1230	T. Hioki, Toyota Central R&D Laboratories, Japan "Tribological Properties of Ceramics Modified by Ion Implantation and by Ion Beam-Assisted Deposition"
1300 - 1600	Labor Day Picnic
2015	Dinner

PROGRAM (continued)--

Tuesday, September 6

CHAIRMAN: A. PEREZ

0830 - 0930	G. K. Wolf, University of Heidelberg, FRG "Chemical Properties of Ion Implanted Ceramics"
0930 - 1000	Break
1000 - 1100	Wolf Continued--
1100 - 1130	Discussion
1130 - 1200	J. Linke, KFA-Julich, FRG "Simulation of Plasma-Induced Material Damage with H- and D-Ion Beams"
1200 - 1230	L. Zhang, University of Sussex, UK "Characterization of Planar Optical Waveguides in Ion Implanted Quartz"
1245	Lunch
1700 - 1730	Coffee/Juice
1730 - 1755	J. E. Pawel, Vanderbilt University, USA "Modified Pull Test for Testing of Adherent Films"
1755 - 1820	W. R. Allen, Oak Ridge National Laboratory, USA Ion Scattering Studies of Helium Implanted into Al_2O_3 and MgO"
1820 - 1845	S. J. Zinkle, Oak Ridge National Laboratory, USA "Ion Irradiation Studies of Oxide Ceramics"
1845 - 1910	L. Clapham, Queen's University, Canada "Ion Beam Studies of High Tc Superconductors"
1910 - 1935	N. Moncroffe, University Claude Bernard. France "Ion Beam Modification of Ceramics"
1935 - 2000	P. A. Scott, University of Illinois. USA "Characterization of Ion Plated Metal Films on Ceramic Substrates"
2030	Dinner

Wednesday, September 7

CHAIRMAN: A. PEREZ

0830 - 0930	P. Townsend, University of Sussex, UK "Effects of Ion Beam Processing on Optical and Electrical Properties"
0930 - 1000	Break
1000 - 1100	Townsend Continued--
1100 - 1130	Discussion
1130 - 1200	C. Buchal, KFA-Julich, FRG "Ion Implantation into $LiNbO_3$"
1215	Lunch
1330	Excursion to Lucca
2015	Dinner

PROGRAM (continued)--

Thursday, September 8

CHAIRMAN: P. MAZZOLDI

0830 - 0930	J. M. Rigsbee, University of Illinois, USA "Plasma- and Ion-Beam-Assisted Physical Vapor Deposition Processes"
0930 - 1000	Break
1000 - 1100	Rigsbee Continued--
1100 - 1130	Discussion
1130 - 1200	T. Bremer, University of Osnabrueck, FRG "Fabrication of Optical Waveguides in $LiNbO_3$ by Ion Implantation"
1200 - 1230	P. Sioshansi, Spire Corporation, USA "A New Spi-Iondep^{TM} Process for Modification of Metallic and Ceramic Surfaces"
1245	Lunch
1700 - 1730	Coffee/Juice
1730 - 1930	F. A. Smidt, Naval Research Laboratory, USA "Ion Beam-Assisted Deposition of Thin Films and Coatings"
1930 - 2000	Discussion
2030	Gala Dinner

Friday, September 9

CHAIRMAN: P. MAZZOLDI

0830 - 0930	A. Anttila, University of Helsinki, Finland "Ion Beam-Induced Diamond-Like Carbon Coatings"
0930 - 0945	Break
0945 - 1045	Anttila Continued--
1045 - 1115	Discussion
1115 - 1245	M. Nastasi, Los Alamos National Laboratory, USA "Ion Beam Modification and Analysis of High T_C Superconductors"
1245 - 1300	Discussion
1300	Lunch
1700 - 1730	Coffee/Juice
1730 - 1830	Summary of IBMM '88 in Japan
1830 - 1900	Summation and Closing
2000	Dinner

Saturday, September 10

Buses to Pisa

EXCURSIONS AND SOCIAL PROGRAM

Sunday, August 28

1900 - 2030 WELCOME DRINK

Monday, August 29

2130 Introduction to Tuscany - a short talk on the history and attractions with a selection of regional wines and cheeses.

Tuesday, August 31

Buses leave for Pisa returning to Il Ciocco for dinner. FREE, but please sign up at conference desk by Tuesday afternoon so we will know how many buses to rent.

Saturday, September 3

All-day trip to Florence. Cost - $25(US) per person. Please sign up and pay by 1800 Thursday so that buses can be ordered. We strongly recommend that you take the bus if you wish to visit Florence even if you have a car. Central Florence is closed to private automobile traffic and parking at sites convenient to the center is a major problem. You will be on your own once the bus reaches the city. Box lunches will be provided by the hotel if desired. We will leave Florence at [illegible] to 1800 and arrive at Il Ciocco in time for a late dinner.

Sunday, September 4

All-day trip to Sienna and San Gimignano. Cost - $25(US) per person. Same comments as for the Saturday trip.

Monday, September 5

1300 - 1600 Labor Day Picnic

Labor Day is a major U.S. holiday that originated to observe the contributions of labor unions to society and the economy. It has become the holiday to denote the end of summer, the return of children to school, and the start of fall activities. It is traditional to observe this holiday with a picnic and outdoor games and sports. We will have such an afternoon (Italian-style) at one of the hotel facilites about 1 km from the hotel. Bus transportation will be provided.

Wednesday, September 7

FREE excursion to Lucca. Please sign up at conference desk by noon, Tuesday, September 6.

Thursday, September 8

Gala Dinner with orchestra for after-dinner dancing.

Note: There will be at least one additional free trip for the accompanying persons.

CALCULATION OF DEFECT PROPERTIES OF CERAMICS

C. R. A. Catlow
Department of Chemistry, University of Keele
Keele, Staffs. ST5 5BG

In these lectures we will aim to review the fundamentals of the defect properties of ceramics and to describe the methods used in calculating defect parameters, including both bulk and surface defects. Applications to understanding stability, transport, and radiation damage in ceramics will also be reviewed.

The first section of the lecture will describe the types of bulk and surface defects of importance in ceramics. The review of methods for calculating defect energies and entropies will follow. Static techniques using Mott-Littleton methodologies will be described. Molecular dynamics methods, appropriate to high temperature ceramics will also be reviewed. Defect calculations require the specifications of interatomic potentials. We will discuss the types of model available for ceramic materials and will attempt to assess the accuracy and reliability of current calculations.

The final section of the lecture will discuss recent applications of the techniques to topics including the defect structure of superconducting oxides, calculation of impurity segregation energies and the investigation of defect reactions in irradiated solids.

ION-BEAM ALLOYING OF CERAMICS AT HIGH TEMPERATURES

I. L. Singer and J. H. Wandass
U.S. Naval Research Laboratory
Code 6170
Washington, D.C. 20375

Metal ions (Al^+, Ti^+) were implanted to high fluences into Si_3N_4 and SiC. Substrate temperatures were either kept near ambient by refrigeration or driven up to approximately 900°C by ion beam heating (i.e., "hot" implantation). Implanted surfaces were analyzed by XPS, Auger, and RBS (composition vs depth profiles) as well as SEM/EDX. As reported previously,[1] hot Ti^+ implantation resulted in considerable redistribution of Si in the implanted Si_3N_4 layer but no significant deviation from the expected Gaussian-like profile in the implanted SiC layer. Hot Al^+ implantation, by contrast, produced a Gaussian-like profile of Al^+ in the implanted Si_3N_4 layer but considerable redistribution of Al in the implanted SiC layer. The solute redistribution observed in the hot implanted substrates is explained in terms of ternary phases diagrams calculated from thermodynamic data.[2]

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[1] I. L. Singer, Surf. Coat. and Technol. 33 (1987) 487-499.

[2] I. L. Singer, R. G. Vardiman, and C. R. Gossett, in Fundamentals of Beam-Solid Interactions, M. J. Aziz and L. E. Rehn, eds., Materials Research Society, Pittsburgh, PA, 1988) 201-206.

DISORDER, RANDOMNESS, AND AMORPHOUS PHASES

P. Mazzoldi
Dipartimento di Fisica dell'Universita, Via Marzolo 8
35131 Padova, Italy
and
A. Miotello
Dipartimento di Fisica dell'Universita
38050 Povo (Trento), Italy

Ordered solids are experimentally well-characterized, and unified theoretical models for structure as well as for transport and relaxation processes are available.

As opposed to regular lattices, a unified picture for disordered solids is not yet available due to the lacking of general unified theoretical concepts, like Bloch's theorem for regular lattices.

Here we want to describe the amorphous state focussing attention to the liquid-glass transition where thermodynamical properties (density, specific heat, etc...) change in a peculiar way with respect to liquid-crystal transition.

Main features emerging from experimental investigations of structural relaxations in glasses will be presented with emphasis placed upon low-frequency excitations whose nature remains up to now quite obscure. In this context harmonic and quasielastic modes as well as two-level states will be discussed.

Transport properties of glasses will be also analyzed paying attention to theoretical models which try to explain ionic motion in disordered solids through cooperative atomic rearrangement. To this purpose recent investigations of radiation-induced enhanced transport processes will be presented. Finally, we try to make a connection between structure and transport properties, having in mind relaxation processes.

THE GENERAL DISPLACEMENT CASCADE IN SOLIDS

Don M. Parkin
Center for Materials Science
Los Alamos National Laboratory
Los Alamos, NM 87545

A general description of the displacement cascade in solids would include elemental composition material stoichiometry, crystal structure, bonding type (metallic, ionic, covalent), temperature, and irradiating particle and energy as principle parameters. At present, no model exists that includes all of these parameters. Over the last forty or so years, a great deal of experimental and theoretical research has focused on this problem. Out of this work, a fairly self-consistent picture of the displacement cascade has evolved but it is limited to rather a small region of the parameter space. The most complete model, for example, exists for displacement cascades of up to a few kiloelectron volts in simple cubic metals at low temperatures. This model is the most generally adopted starting point for describing the more general case of the displacement cascade.

In this lecture we will present a description of the displacement cascade that includes elemental composition, material stoichiometry, bonding type, and irradiating particle and energy. The model will be presented as a generalization of the widely accepted Kinchin and Pease formulation as modified by Norgett, Robinson, and Torrens. A generalization of the damage energy and the total and net displacement functions will be introduced. Computer calculations will be used to study the importance of displacement threshold behavior, elemental mass ratio, material stoichiometry, bonding type, and irradiating particle and energy. It will be shown that general behaviors can be described and modeled, but that no universal formula is obtainable.

The specific problem of ion irradiation of ceramics will be addressed with both computer modeled results and experimental results from the literature. Specific examples that apply to the exciting new ceramic oxide superconductors will be discussed.

ENHANCED HARDNESS AND WEAR RESISTANCE IN POLYMERIC CARBONS BY ION IMPLANTATION

John T.A. Pollock
CSIRO Division of Materials Science and Technology
Lucas Heights Research Laboratories
Private Mail Bag 7
Menai, NSW, 2234, Australia

Polymeric carbons are formed by heating high molecular weight polymers to temperatures where the non-carbon content is lost as gas and the resulting carbon mass has a 'tangled' largely graphitic microstructure which relates to the polymer chain configuration. These carbons include fibers, glassy carbon and many of the chars. Recent work from our laboratory is reviewed dealing with the potential of ion implantation as a modification tool for improving the surface mechanical properties of these carbons.

Major emphasis is placed on the implantation and subsequent characterization of glassy or vitreous carbon, although data is presented supporting the general applicability of implantation for the enhancement of the mechanical properties of graphite-based carbons. Wear resistance has been measured, using both diamond abrasion and sliding ruby ball-on-disc, as a function of implant species, energy, and dose. Nuclear reaction analysis based on the $^{15}N\ (P,\alpha)^{12}C$ reaction indicates that the modified layer is 400X more wear resistant to 1 μm diamond abrasion than the unimplanted material. Data analysis together with TRIM calculations provide support for the hypothesis that ion damage is the principal mechanism operating. The microstructural changes accompanying the implantation have been examined using TEM and Raman spectroscopy. These results are discussed together with wear resistance and ion damage modelling data, although interpretation is not yet clear.

The potential value of the enhanced surface properties is discussed with regard to current and proposed use of these materials in structural, electrical, and bio-engineering applications.

PROPERTIES OF IRON IMPLANTED DIAMOND

J. A. Sawicki,[1] B. D. Sawicka,[1] and H. de Waard[2]

[1]Chalk River Nuclear Laboratories, Chalk River, KIOJ1JO Ontario, Canada
[2]University of Gronigen, NL-09718CM, Gronigen, The Netherlands

Because of its numerous extraordinary properties such as the closest atomic packing, extreme hardness, high melting point, high heat conductivity, low electrical conductivity, large forbidden gap, large refraction index, etc., diamond, and especially diamond films, are considered to be materials of the future. Diamond, having the highest known Einstein and Debye temperatures ($\theta_E \approx 1320$ K and $\theta_D \approx 2230$ K at 0 K), can also be considered a unique host material for Mossbauer spectroscopy sources characterized by very high recoil free factors.

We performed a series of Mossbauer spectroscopy measurements on ion implanted ^{57}Fe (stable) and ^{57}Co (radioactive) diamond specimens. The fluence of the implanted ions varied between 10^{12} and 10^{17} atoms/cm^2 and the ion energies ranged from 30 to 100 keV. The target temperature during implantation was either 300 or 800 K.

Two different regions of ion fluences were identified. Above a fluence of about $2 \cdot 10^{13}$ atoms/cm^2, the Mossbauer spectra represent Fe impurities in an amorphized surrounding, similar to the case of Fe implantation into graphite. Below about $2 \cdot 10^{13}$ atoms/cm^2, Mossbauer spectra indicate a superposition of amorphous-like regions and crystal-like regions. The fraction of the impurity atoms located in the crystal-like regions was about 5% in the sample implanted at room temperature, and increased up to about 20% by annealing or by making the implantation at 800 K.

Iron atoms in a crystal-like surrounding were found to have unique properties. First, they exhibit a single Mossbauer line (cubic symmetry) and a very large negative isomer shift (high s-electron density). Next, they exhibit a very high recoil-free factor (effective Debye tempeature 1300 K).

ION ENERGY DISSIPATION AND SPUTTERING DURING BOMBARDMENT OF MULTICOMPONENT MATERIALS

Jorgen Schou
Physics Department
Association EURATOM, Riso National Laboratory
DK-4000 Roskilde, Denmark

The energy loss processes during ion slowing-down are closely connected to damage production and sputtering for both pure elements and multicomponent materials. The general behavior of the stopping power of pure elements is known relatively well, although there exist ion-target combinations and energy regimes, for which the stopping power predictions are uncertain.

A complicating feature for multicomponent targets is the deviation of the electronic stopping power from the additivity of the stopping power of the constituents, the so-called Bragg's rule. The deviations are largest for elements of low atomic number and for low-energy projectiles.

The energy loss to the nuclei described by the nuclear stopping power leads to knock-on (ordinary) sputtering, in which target particles are ejected as a result of the collisions initiated by the primary. The behavior of the sputtering yield for multicomponent targets is generally much less known than the yield from pure elements. For multicomponent materials a number of additional parameters, for example the primary ion fluence and the concentration of the components, influence the sputtering.

Sputtering via electronic transitions takes place for insulating materials, in which the kinetic energy for the particles in motion stems from electronic deexcitations to repulsive states. This electronic sputtering may be correlated to the electronic stopping power in analogy with the connection between knock-on sputtering and nuclear stopping power. Electronic sputtering has been explored very little compared to knock-on sputtering. It seems likely that no universal mechanism is responsible for electronic sputtering, but that the mechanism depends strongly on the particular type of the material and of the primary particles.

MECHANISMS OF ION BEAM MIXING

F. W. Saris
F.O.M. Institute for Atomic and Molecular Physics
Amsterdam, The Netherlands

The slowing down of energetic ions in a solid and the evolution of disturbances are transient processes. The prompt regime, lasting about 10^{-11} s, refers to the period from the initial ion impact up to the time required to establish a uniform ambient temperature throughout the solid. During this period, two limiting kinds of events contribute to the mixing. As the energetic ions penetrate a solid, they transfer part of the kinetic energy by colliding with target atoms in primary collisions. These atoms recoil and collide with other atoms in secondary collisions. The later-generation collisions produce many low energy recoils, which induce small displacements in random directions. This process is often called cascade mixing. A small fraction of the atoms are mixed by the primary anisotropic recoil events at high energy. The resulting relocation is called recoil mixing.

At the end of the prompt regime, the collision cascade will have generated a nonequilibrium number of defects. If the ambient temperature is sufficiently high, these defects can be mobile, causing more diffusion and mixing. This "radiation-enhanced diffusion" is temperature dependent.

Ion mixing phenomena have been described traditionally by ballistic models. Recent investigations, however, suggest that thermochemical effects are often important. Large variations in mixing between systems that have similar collisional characteristics emphasize the need to take into account the heat of mixing. A direct correlation between the mixing rate of bilayers and the cohesive energy of the corresponding elements has been established. These thermodynamic effects are especially important in the late stages of the prompt regime, during the thermal spike. In the thermal spike the velocity distribution of moving particles resembles the Maxwell-Boltzmann distribution and the concept of a local temperature can be introduced through the use of the law of equipartition of energy. The temperature can be calculated from the thermal diffusion equation under specific conditions. A phenomenological description of ion mixing has been developed in which the heat of mixing effect and the cohesive energy effect are incorporated in the thermal spike idea.

Finally, one of the most interesting results of ion mixing is the formation of metastable phases. The structural character of ion-induced phases can be correlated to the properties of the constituent elements and the equilibrium phase diagrams.

ION BEAM MIXING OF Fe IN SiO_2: STRUCTURAL AND OPTICAL PROPERTIES

G. Battaglin,[1] S. Lo Russo,[1] A. Paccagnella,[2]
P. Polato,[3] and G. Principi[4]

[1]Dipartimento di Fisica, via Marzolo n.8, 35131 Padova, Italy
[2]Dipartimento di Ingegneria, 38050 Mesiano di Povo (TN), Italy
[3]Stazione Sperimentale del Vetro, via Briati 10, 30121 Murano (VE), Italy
[4]Dipartimento di Ingegneria Meccanica, Sezione Materiali, via Marzolo 9, 35131 Padova, Italy

Iron films e-beam evaporated onto fused SiO_2 have been irradiated with 200 keV Kr ions in the dose range $3.6\cdot10^{14}$ to $1.3\cdot10^{17}$ cm^{-2}. Different film thicknesses (in the range 10 to 80 nm) have been used. The Fe mixed amounts have been measured by RBS and surface morphology modifications have been monitored by SEM.

The mixing effect has been studied in more detail as a function of the Kr dose for a 40-nm-thick Fe film. Two mixing regimes have been observed: for doses up to $3\cdot10^{15}$ cm^{-2} there is a linear relationship between the Fe mixed amount and the Kr dose. At higher doses, the mixing efficiency decreases, suggesting the presence of demixing phenomena. SEM analyses show the formation of holes in the Fe film for Kr doses higher than $3\cdot10^{16}$ cm^{-2}.

Mössbauer spectroscopy analyses show states of different coordination for Fe in the SiO_2 matrix: metallic Fe in the form of small clusters, FeO-like oxide and Fe-silicates are formed in different relative amount depending on the bombarding ion dose.

Optical measurements show that the reflectivity of the mixed samples increases in the visible and U.V. regions and reduces in the I.R. region. This effect increases with the amount of mixed Fe. Samples containing the highest amount of Fe display also a noticeable increase in the absorption coefficient in the U.V. and visible regions.

DYNAMIC ION IMPLANTATION STUDIES IN THIN CERAMIC FILMS

Ivette Oppenheim and K. R. Padmanabham
Department of Physics and Astronomy
Wayne State University
Detroit, MI 48202

The feasibility to deposit ceramic films by dynamic implantation technique is discussed. In this technique, energetic reactive ion species implanted during film deposition can initiate recoil implantation of atoms from the concurrently deposited film into the substrate followed by mixing or precipitation of the implanted species into the film. By appropriate choice of the ion to atom arrival ratio, the technique of dynamic implantation may be employed to deposit thick ion beam modified ceramic films by sputter deposition from metal targets. Examples of the use of the technique in the preparation of nitride, carbide and boride films of group IV-B metals and i-C films are presented. The modification in mechanical properties of the films deposited by dynamic implantation technique are compared to those prepared by post-deposition implantation method. The effect of ion to atom arrival ratio on the extent of atomic mixing achievable from the film-substrate interface will be discussed by comparing the calculated ion concentration profiles with those measured experimentally. The changes in the structure and composition of the films and their effect on mechanical properties will be presented. This work is partially supported by the Institute of Manufacturing Research, Wayne State University.

DEFECT CREATION IN ION BOMBARDED INORGANIC INSULATORS

P. Thevenard
Universite Claude Bernard Lyon I
Departement de Physique des Materiaux
63 Bd du 11 Novembre 1918
69622 Villeurbanne, France

In this lecture, after a brief review on defects in ionic crystals, the intrinsic defect creation in alkali halides and simple oxides (MgO, TiO_2) is described with regard to particule-matter interaction. The track effect associated with electronic interaction in the case of high energy particles and the atomic collision processes preponderant at low energy are used to interpret the defect creation in alkali halides and oxides respectively. Finally, the aggregation and precipitation mechanisms responsible for new phase formation in inorganic insulators are presented and discussed taking into account the high energy deposition and the high concentrations of defects characteristic of ion bombarded solids.

STRUCTURAL PROPERTIES OF IRON IMPLANTED ZrO_2

J. A. Sawicki, G. Marest,[1] B. Cox, and B. D. Sawicka
Chalk River Nuclear Laboratories
Chalk River, Ontario KOJ 1JO, Canada

Zirconium oxide is an important constituent of advanced tough ceramics, solid electrolytes, oxygen sensors, catalysts and nuclear cladding materials. In order to understand the chemical interaction of ZrO_2 with energetic transition metal ions, zirconium oxide targets implanted with ^{57}Fe ions at an energy of 100 keV and at fluences in a range 10^{15} to 10^{17} ions/cm^2, have been examined by conversion electron Mossbauer spectroscopy. The variation of valent states of iron, from mostly ferric Fe^{3+} state at low doses, through superposition of Fe^{3+} and Fe^{2+} states at intermediate doses, to metallic Fe^0 and Fe^{3+} mixture of states at high doses was established. The oxidation states of iron in sintered zirconia targets and in anodically and thermally prepared ZrO_2 films have been compared, and the influence of annealing treatment has been studied. The near-surface chemical properties of iron-implanted zirconia differ considerably from those for thermally doped zirconia.[2] Similarities between Fe-ZrO_2 and the earlier studied Fe-MgO system[3] will be discussed.

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[1]Institut de Physique Nucleaire, Universite Claude Bernard, Lyon I, F69622, Villeurbanne, France.

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MICROSTRUCTURAL CHARACTERIZATION OF ION BEAM MIXED Al_2O_3/Cu INTERFACE - APPLICATION TO ADHESION

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The problem of adhesion at the interface between non-reactive materials such as metal-ceramics is a subject of growing interest taking into account the large field of potential applications. The conventional techniques such as thermo-compression which are used to improve the bonding at the interface need generaly some very hard experimental conditions (i.e., high temperature) which are not always applicable to specific systems. A "cold" technique such as the ion beam mixing technique which acts at the interface in non-equilibrium conditions can be an interesting way to enhance adhesion in the case of immiscible and non-reacting materials. In this context, copper films, the thickness of which was between 10 and 100 nm, was deposited, using e-beam evaporation in a vacuum system (10^{-7} torr), on the polished face of sapphire platelets. The ion beam mixing was performed at room temperature using 1.5 MeV Xe^+ ions and doses ranging from 10^{15} up to 2.10^{16} ions/cm^2. The mixing effect at the interface was characterized by Rutherford backscattering analysis (RBS) associated with high resolution transmission electron microscopy (HREM) observations on cross section samples. These measurements show that the mixing effect concerns a thin zone at the interface (~3 to 5 nm). Under this zone a heavily damaged region in the sapphire substrate down to the stopping zone of Xe^+ ions is observed. Peel tests for adhesion correlated with the mixing conditions and the results of the physicochemical and microstructural characterizations will be discussed.

ION BEAM-INDUCED CRYSTALLINE TO AMORPHOUS TRANSFORMATIONS IN CERAMIC MATERIALS

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Since it has been emphasized that the role of lecturers at this NATO Advanced Study Institute is tutorial, I plan to spend the early part of this talk on a description of the physics of ion implantation. The essential features of ion sources, magnetic separation and acceleration of the ions into the target will be discussed.

Harking back to the early experiments of some two decades ago, crystalline to amorphous transitions in ion implanted ceramic single crystals were studied by reflection electron diffraction and gas release measurements. Radiotracers and precise sectioning techniques were utilized which enabled the determination of range profiles within the targets. Range profiles could be measured as a function of incident beam energy, type of ion, and, more importantly, beam fluence, the combination of which dictated the onset of crystalline to amorphous transitions. These experimentally determined profiles can now be compared with more recent computer-generated distributions which give the projected range (Rp) as a function of implant energy.

It should be realized that the wide range of crystal structures and bonding characteristics of ceramics results in more complex mechanisms of crystalline to amorphous transitions than those observed in metals and monovalent semiconductors. This will be discussed in light of the comparative stability under ion bombardment of materials with cubic and non-cubic crystal structures. Earlier findings will be compared to more recent results obtained by the techniques of Rutherford backscattering combined with channelling of MeV +He ions and with secondary ion mass spectrometry (SIMS).

COMPOUND FORMATION AND CHEMICAL FACTORS IN ION BEAM AND LASER TREATMENTS

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Surface composition changes have long been documented with ion bombarded alloys, oxides, and oxysalts. Corresponding experiments with laser pulses have been less detailed except for those involving some aspect of the removal of surface layers. The basic question that we ask in each case is: What is the mechanism of the composition change? The history of understanding these effects is interesting, in that prior to about 1983 ion beams were assumed to act either collisionally or thermally, and laser pulses were assumed to act only thermally, often with unexplained complications. We now know that ion beams act collisionally only with isotopes or near the threshold, that they soldom give clear evidence for thermal effects, that with the majority of alloys such composition change as occurs is triggered by Gibbsian segregation, and that with the majority of oxides and oxysalts there are identifiable roles played by the surface binding energy and by energy minimization in the collision cascade. The unifying feature is the predominance of processes driven by <u>chemical energy differences</u>.

Likewise, we now know that the apparent importance of thermal effects with laser pulses, often accompanied by complications such as particle temperatures which differed from the surface temperature, was the result of faulty data analysis. Laser sputtering differs from ion-beam sputtering in that, since emission is confined to a short interval of time (often 10^{-8} s), the number density of emitted particles is transiently very high, near-surface collisions occur, and a so-called <u>Knudsen layer</u> forms. Knudsen-layer formation can be taken into account <u>analytically</u> and, when this is done, the composition changes turn out to be due either to a thermal mechanism or (until recently unsuspected) to chemical bond disruption. There tend to be no complications such as those relating to the particle temperature.

ION BEAM MIXING OF METALS AND CERAMICS – MATERIAL CONSIDERATIONS*

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The contributions of both physical and chemical (thermodynamic) processes to ion beam mixing are understood for systems involving two or more metallic species. The physical processes include ballistic mixing, radiation-enhanced diffusion (RED) and radiation-induced segregation (RIS) controlled by the radiation-induced defect concentrations. The thermodynamic property found to be most important is the chemical heat of mixing.

The situation is more complex and less understood for ion beam irradiation of a metal/compound system. The recoil of metal atoms (ions) into the compound produces a change in the stoichiometry, generally introducing an excess number of cations to anions. Depending on the nature of the compound, complex defect states may be created and these may greatly affect RED and RIS. The driving force for de-mixing may also be quite high. Attempts to predict whether or not mixing will occur using simple thermodynamics, arguments based on the reaction enthalpy have been only partially successful.

In this lecture, a review of experimental observations will be followed by a discussion of current models of possible mechanisms.

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ION IMPLANTATION IN ZIRCONIA

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Ceramic solid solutions of $(1-x)ZrO_2$ - x $YO_{1.5}$ with x = .14 were implanted with high doses of Fe, Ti, and Ag. The microstructure of the implanted layer was studied by Scanning Transmission Electron Microscopy (STEM).

Implantation of the cubic zirconia with 50 keV Ag up to a dose of 8×10^{16} at. cm^{-2} resulted in the amorphization of the lattice. Microstructural changes due to thermal annealing will be discussed.

Implantation with 15 keV Fe up to a dose of 8×10^{16} at. cm^{-2} caused no amorphization but a recrystallization of the lattice. A substructure in the original ceramic grains resulted from the implantation process.

The effect of the implanted ion on the electrical properties will also be discussed.

If no experimental problems have occurred, then also some hardness measurements of N implanted tetragonal zirconia will be presented.

ION BEAM MIXING AND ANNEALING OF METAL/Al_2O_3 STRUCTURES

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The study is concerned with the evolution of the interfacial energy of thin metallic films evaporated on alumina and submitted to xenon irradiation. The ion energy was 1.5 MeV and the fluence ranged from $3 \cdot 10^{15}$ to $2 \cdot 10^{16}$ $Xe \cdot cm^{-2}$. The samples were irradiated at temperatures of 77 and 300K. Thermal annealing treatments at temperature near one half of the melting point of the metal have been performed in order to study the irradiation effects on the interfacial energy of the metal/Al_2O_3 structures.

The interface modification has been characterized by different techniques such as Rutherford backscattering spectrometry (RBS), scaning and transmission electron microscopy (SEM and TEM, respectively), optical absorption, x-ray diffraction at glancing incidence and electrical resistivity measurements.

The influence of the alumina structure on the interface modification has been studied by using either single crystal (α-Al_2O_3) or amorphous evaporated alumina film (a-Al_2O_3).

Two metals have been selected for this study taking into account a thermodynamical criterion: silver and niobium which present quite different chemical reactivities with Al_2O_3.

Blistering of amorphous alumina appears for Xe bombardment at fluences as low as $3 \cdot 10^{15}$ $Xe \cdot cm^{-2}$. Such bubble formation is not obtained in the case of sapphire. Excepted this topographic effect, the behaviors of a metal/a-Al_2O_3 and metal/α-Al_2O_3 are quite similar.

For Ag/Al_2O_3 samples subjected to Xe irradiation, a high lateral segregation of the silver film is observed without evidence of an interdiffusion of two materials at the interface. Thermal annealing of the unirradiated and irradiated samples do not reveal any important modification of the interfacial energy.

CHANGING THE MECHANICAL PROPERTIES OF CERAMICS BY ION IMPLANTATION

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Since ion implantation is a means of modifying the near-surface region of materials, it is to be expected that the most obvious behavioral changes will be those associated with properties such as hardness, friction, and wear. While this is found to be the case, implantation may also affect some bulk properties which are also surface-sensitive; for example, slow crack growth, fatigue and strength. Implantation may also be an important ancillary process in using thin surface coatings by modifying the structure of the coating and improving adhesion.

The magnitude of observed changes in indentation hardness response depend on the depth of the indentations used compared to the scale of the implantation-affected layer. Typically, hardness increases with the radiation damage and solid solution structures introduced during implantation and reaches a maximum at the onset of structural amorphization. Once formed, amorphous material – which tends to be much softer than the parent crystal – tends to dominate the composite hardness response of the surface. Further effects on hardness can be achieved by heat treatment of the implanted surface to produce a precipitation-hardened or composite-like near-surface structure.

Both radiation damage and the implanted species themselves can introduce very large compressive stresses into the near-surface layer and these can have marked effects on fracture behavior. Such effects can also be more complex such as the consequences of implantation on the deformation response of MgO and the toughness behavior of partially stabilized zirconias.

Friction is also found to be affected by implantation, though at least two mechanisms may be operating. The first is the removal of chemisorbed water and other impurities from oxide ceramic surfaces leading to marked increases int he coefficient of friction with both ceramics and metal contacts. Implantation also inhibits the reabsorption of water over very long periods of time, possibly resulting from the changed near-surface charge state. This same change in near-surface charge state may also have other effects in the friction response.

Examples of these effects will be discussed as will the differences in behavior observed between various single crystal ceramics, polycrystalline engineering forms of ceramics and glasses.

TRIBOLOGICAL PROPERTIES OF ION BEAM MODIFIED CERAMICS AT ELEVATED TEMPERATURES

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The problems of friction and wear at mating ceramic surface have been receiving increased attention, in step with the expanding field of applications for structural ceramics components. One avenue for the optimization and possible tailoring of ceramic surfaces wearing at high temperatures is through the utilization of high energy deposition schemes. Friction and wear are secondary to multitude of parameters, intrinsic and extrinsic, which come together to dictate the dynamic behavior of a particular system. We first review, briefly, these parameters against the background of prevailing friction and wear theories. We then discuss, specifically, the evolution of friction and wear with temperature, with emphasis on adhesive wear. The paper concludes with a review of surface modification schemes and how they affect the tribological behavior of ceramic materials.

THIN FILM AND NEAR-SURFACE CHARACTERIZATION USING A MECHANICAL PROPERTIES MICROPROBE*

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An ultralow load microindentation system will be described and examples of its applications given. The system's spatial resolution and its data acquisition capabilities allow the determination of several mechanical properties from volumes of material with submicron dimensions. Research with this instrument has led to improved techniques for determining the plastic and elastic properties of materials from microindentation experiments. The techniques have been applied to thin layers created by ion implantation of metals and ceramics, radiation damaged materials, and thin hard coatings. Changes in hardness and modulus of elasticity have been measured in films as thin as 100 nm.

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TRIBOLOGICAL PROPERTIES OF CERAMICS MODIFIED BY ION IMPLANTATION AND BY ION BEAM-ASSISTED DEPOSITION OF ORGANIC MATERIAL

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To improve the tribological properties of ceramics, two techniques for modifying the ceramics surface were employed: the implantation of energetic ions and the formation of a solid carbonaceous film onto the ceramics surface by vapor deposition of an organic material and simultaneous ion irradiation. The friction and wear properties of the modified ceramics were tested by using the pin-on-disk method. The ceramic materials studied were SiC, Si_3N_4, and Al_2O_3.

The results obtained are as follows:

(1) The sliding friction coefficients (μ's) between steel pins and a polycrystalline SiC disk are reduced from 0.6 to 0.15 by implanting Ar^+ or Ag^+ ions into the disk. The durability of the low μ state is more than 1×10^5 cycles for a disk implanted with Ar^+ ions at 800 keV to a dose of 1×10^{16} ions/cm^2.

(2) An adhesive solid carbonaceous film can be formed on the ceramic substrates by the vapor deposition of a silicone oil (pentaphenyle-trimetyle-trisiloxane) and simultaneous 1.5 MeV-Ar^+ ion irradiation. The coated disks in sliding contact with Si_3N_4 or SUJ2 steel pin show friction coefficients as low as 0.04 to 0.1. The low friction coefficient persists up to 1×10^5 cycles for a Si_3N_4 disk coated with a 0.2 μm-thick film.

These results are discussed in relation to the structure of the modified surface layer.

CHEMICAL PROPERTIES OF ION IMPLANTED CERAMICS

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The contribution will deal with the chemical aspects of ion bombardment of ceramics. Ion implantation, ion beam mixing and ion beam-assisted deposition will be covered from a chemical point of view. The first "basic" section will deal with radiation chemistry and "hot atom" chemistry of ceramics- and insulator-surfaces and metal/ceramic-interfaces under bombardment. The second "main" section is intended to give a survey on potential applications of ion beam-treated ceramics and some other insulators in chemistry and on chemical processes occurring at modified materials. Especially the following subjects will be treated:

- Catalytical application of modified ceramics
- Corrosion of modified ceramics
- Modification of conductive ceramics
- Metal coatings on ceramics and their catalytic and corrosion behavior
- Ceramic coatings on metals and their catalytic and corrosion behavior

In the last section, the future development with respect to the subjects mentioned, and the necessary research will be discussed. Finally, the potential of ion beam modification of ceramics will be compared with other techniques.

SIMULATION OF PLASMA-INDUCED MATERIAL DAMAGES WITH H- AND D-ION BEAMS

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Plasma wall interaction is a denomination for several sub-processes affecting the surface of the plasma-facing components in a thermonuclear fusion reactor. Here besides electromagnetic radiation, arcing, and neutron irradiation, two processes may play a life-limiting role for the so-called first wall, namely thermal fatigue by the pulsed operation of a Tokamak and thermal shock loading by plasma disruptions or run-away electrons during unstable plasma states.

In order to determine the load limits for these two loading types for various first-wall materials, systematic series of material tests have been carried out. To simulate the thermal load to the first-wall primarily energetic electrons (e.g., in an electron beam welding machine) are used in different laboratories worldwide. In these tests the critical thermal loads for surface modifications such as erosion, grain growth, crack formation, melting or sublimation are determined. Besides the quantification of the resulting damages, it is of significant importance to improve the thermo-mechanical performance of the materials.

The materials tested so far range from metallic alloys (e.g., Fe- or Ni-based alloys, refractory metals) to graphites and ceramic materials. Since first-wall components with high atomic numbers (Z) are generally undesired from the plasma-physical viewpoint, non-metallic materials are the prime candidates for the inner wall of the next generation plasma machines. Graphites and especially ceramics are very sensitive to thermal shocks (e.g., by disruptions or run-away electrons); to meet the needs for a better thermal shock resistance of these materials different types of fiber-reinforced grades have been tested successfully.

CHARACTERIZATION OF PLANAR OPTICAL WAVEGUIDES IN ION-IMPLANTED QUARTZ

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Planar optical waveguides have been made by ion implantation in Y-cut quartz using He^+ ions of energies 0.7 to 2.2 MeV with doses from 5×10^{15} to 1.6×10^{17} ions/cm^2 at 300 and 77K. These waveguides rely on the formation of a low index optical "barrier" a few microns below the surface caused by a physical reduction in density where the ions undergo their final stages of decelleration (nuclear stopping). A detailed analysis of the complete index profiles (including barrier shape) has been made for both ordinary index n_o and extraordinary index n_e from the experimentally measured dark mode spacings (at 0.6328 and 0.488 µm), and achieved by means of our recently developed technique involving a reflectivity calculation which assesses the positions of all real and apparent dark modes. The results show that a skewed Gaussian barrier is produced which saturates at $-\Delta n$ ~5% for a dose ~10^{16} ions/cm^2 and thereafter broadens to give a very effective guide confinement. Practically no index change occurs in the guiding region. The thermal stability has been tested to above 1000°C.

Attenuation has been measured using a method similar to the three prism technique. The main causes of loss in these guides are barrier tunneling, color center absorption, inhomogeneous scattering and surface scattering. We have optimized the barrier for low tunneling loss (at a width of 0.8 µm for dose 3×10^{16} ions/cm^2) and subsequent color center annealing has further reduced this value (<1 dB/cm after 500°C). The residual loss is attributed mainly to surface scattering and this has been partially corrected by post-implant polishing, and also by subsequent implants at very low energy (~0.2 MeV O^+) to confine the guide away from the surface.

MODIFIED PULL TEST FOR THE TESTING OF VERY ADHERENT FILMS*

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In principle, the pull test is the most straightforward of the many quantitative adhesion measurement techniques. In practice, however, it is not so easily used. Because the adhesion strength of the film to the substrate is often greater than that of the epoxy or cement to the film, crack nucleation at the film/substrate interface can be difficult to achieve. In this work, a thin, non-wetting film was sputter-deposited onto a portion of the test surface before the subject film was vapor-deposited. The region of the test film that overlapped the non-adherent layer provided a well-defined, reproducible crack that lowered the apparent adhesion of the film to within the range of the pull-tester and forced crack propagation along the film/substrate interface. This configuration corresponds to Mode I crack opening. The bond strength between the subject film and substrate was expressed in terms of a stress intensity factor. An example of the use of this test for zirconium films on sapphire substrates will be given.

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ION SCATTERING STUDIES OF HELIUM IMPLANTED IN ALUMINA AND MAGNESIUM OXIDE*

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Synergies between helium produced by transmutation reactions and displacement damage contribute to dimensional instability and mechanical property degradation in metals and alloys subject to a neutron-rich environment. Phase transformations, embrittlement, and swelling strongly correlate with helium mobility in the material. Theory and isolated experimental data suggest that similar mechanisms may operate in ceramic oxides. While reliable data for helium mobility in some metallic alloys is available, there is virtually no information concerning helium behavior in ceramics of interest. The lattice location and diffusion of ion implanted helium in various ceramics has been investigated by ion beam analytical techniques.

Single crystals of alumina and magnesium oxide were implanted with 200 keV helium at temperatures ranging from 25 to 800°C. The possible occupation of helium in a preferred lattice site was examined with nuclear reaction microanalysis and ion channeling. A significant fraction of the helium implanted in alumina was determined to reside in an octahedral lattice location for all implant temperatures. The fraction of the total helium located in this site was found to range from 56 to 80%, depending upon implant temperature. A rapid migration of helium from the range peak was noted in the concentration profile for the 800°C implant. Similar implants in magnesium oxide showed no evidence of either helium residency in a unique lattice location or rapid diffusion. This divergent behavior may be explained by differences in the lattice structures.

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ION IRRADIATION STUDIES OF OXIDE CERAMICS*

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Ion implantation is a useful tool for modifying the surface properties of ceramic materials. Unfortunately, the fundamental processes responsible for the surface modification are not well understood due to the complex interaction between chemical (implanted ion) effects and radiation damage effects. One approach that may be used to separate these effects involves the use of high-energy ions. Under suitable conditions, it is possible to obtain ceramic specimens that exhibit only displacement damage effects at depths corresponding to about half the ion range. The regions at depths near the ion range are affected by both displacement damage and injected ion effects. A comparison of the microstructures in these two regions can provide information about the relative importance of chemical versus displacement damage effects on surface modification.

Polycrystalline specimens of Al_2O_3, MgO, and $MgAl_2O_4$ have been irradiated with Mg^+ ions or a combination of Al^+ and O^+ ions (Al_2O_3 specimens only) to fluences of 3×10^{19} to 1.5×10^{21} ions/cm^2. The ion energies were about 1 MeV in all cases. The corresponding ion ranges were about 1.5 μm. The irradiations were conducted at room temperature and at 650°C. Transmission electron microscopy was performed on cross-sectioned specimens so that the depth-dependent microstructure could be observed. Dislocation loops were formed for all cases, although their size and density were strongly dependent on the material and the irradiation conditions. For example, spinel specimens irradiated at 650°C had a loop-denuded zone within about 1 μm of the surface whereas the 25°C specimen contained loops in the near-surface region. Some limited mechanical property measurements using a specialized low-load hardness tester will also be described.

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ION BEAM STUDIES OF HIGH T_C SUPERCONDUCTORS

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Abstract not available.

ION BEAM MODIFICATION OF CERAMICS

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CHARACTERIZATION OF ION-PLATED METAL FILMS ON CERAMIC SUBSTRATES

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Elemental Cu and multilayer Cr/Cu films have been deposited onto glass ceramic substrates using an ion plating technique. The coating growth morphologies and interface microstructures are related to the materials processing parameters. Characterization techniques include TEM, SEM, and AES.

EFFECTS OF ION BEAM PROCESSING ON OPTICAL AND ELECTRICAL PROPERTIES

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Major property changes can result from ion implantation of insulating material. Modifications of optical, chemical, and mechanical performance are all well documented. In general it is convenient to separate effects produced by nuclear collisions and electronic excitation. In crystalline targets one assumes that the nuclear collision damage will destroy the long range order of the lattice and the consequent reduction in density will be accompanied by a reduction in refractive index. By contrast the electronic excitation may cause no obvious damage, as in quartz; lead to index enhancement, as in BGO; or index reduction, as in n_0 of $LiNbO_3$. Factors of ion movement, radiation enhanced diffusion, relaxation into new phases, etc., will be discussed.

For amorphous material, there are similar difficulties in predicting the magnitude of the changes induced. Nevertheless in a wide range of materials one can generate optical waveguides with valuable features of low loss, stability, resistance to optical damage at high laser power levels and only minor reductions in electro-optic properties. One may combine the damage techniques with layers formed by diffusion doping or epitaxial growth. Additionally, the major changes in chemical reactivity can be used to define topographic features.

A major advantage of ion beam processing is that it may be performed at low temperatures and many of the key materials for electro-optics have low temperature phase transitions so are not suitable for high temperature processing (e.g., by diffusion).

The talk will also include speculation on the role of ion beam processing for laser development as the movement to compact solid state tunable crystal lasers is ideal for waveguide lasers realized by ion implantation.

ION IMPLANTATION INTO $LiNbO_3$

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$LiNbO_3$ is the best substrate for modulators and switches for integrated optics. Efficient low loss waveguides for light in $LiNbO_3$ are formed by introducing Ti-ions into its lattice, thus increasing locally the ordinary and the extraordinary indices of refraction. We are the first to use the very versatile technique of non-implantation to administer Ti into $LiNbO_3$. This implantation process offers the possibility to introduce significantly more Ti into a well-defined volume than conventional diffusion techniques. During this process first an amorphous non-equilibrium phase is generated, which has to be kept at low temperatures in order to prevent segregation. Subsequent thermal treatment leads to solid phase epitaxy and restores the desired stable crystalline state. We have used this technique to fabricate excellent planar waveguides, channel waveguides, and Mach-Zehnder modulators.

PLASMA- AND ION-BEAM ASSISTED PHYSICAL VAPOR DEPOSITION PROCESSES AND MATERIALS

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Bombardment of a physical vapor deposited (PVD) film with energetic particles (ions and neutrals) prior to and during film deposition can dramatically and beneficially alter the structure, chemistry, and physical properties of the film and the film/substrate interface. Applications of plasma-assisted and ion beam-assisted thin film PVD processes are increasing in such areas as microelectronics and aerospace where improved performance requirements are continually being placed upon materials. Such energetic particle bombardment has also been found to enhance formation of new materials and alloys, such as compound semiconductors, which have metastable microstructures and unique properties.

The objectives of this presentation are to review (1) the processes for plasma and ion beam-assisted physical vapor deposition and (2) the structure, chemistry, and physical properties of films deposited with these processes. Discussion will include ceramic (nitride and oxide), metallic (elemental and layered), and compound semiconductor films deposited onto metallic and ceramic substrates. Topics to be discussed include the effects of energetic particle bombardment on film characteristics such as: porosity; residual stresses; grain nucleation, growth, and preferred orientation; and, adhesion, including chemical mixing and compound formation at the film/substrate interface. Emphasis will be placed on the microstructural (cross-section TEM) and microchemical (EDX, Auger,and SIMS) effects of energetic particle bombardment.

FABRICATION OF OPTICAL WAVEGUIDES IN $LiNbO_3$

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$LiNbO_3$ is one of the preferred substrate materials for integrated optical devices. It has excellent nonlinear properties, and relatively large single domain samples are available at low cost. There are various ways to produce low loss waveguides for near infrared and visible light: titanium induffusion, lithium outdiffusion, proton exchange, ion implantation, and combinations of these techniques.

By varying ion species, dose, and energy, a manifold of profiles can be generated by means of ion implantation. We produced various waveguides which have been implanted with He, Ar, and Ti at energies up to 3.4 MeV. Titanium implantation and ion beam mixing are compared with the proven He implantation. The latter method lowers both refractive indices considerably in the region of ion deposition. The modes are guided between the surface and this barrier. Implantation of transition metal ions produces waveguides with increased refractive index near the surface after suitable annealing procedures.

The effective indices N_m of guided modes m = 0,1, ... were measured by dark-line and bright-line spectroscopy using the prism coupling method. Refractive index profiles were reconstructed with an improved inverse WKB algorithm which gives reliable information about monotonously decreasing profiles. By measuring the refractive index profile alterations after stepwise annealing, we got information about restorage of crystal properties. In some cases of heavy ion implantation, the substrate was totally amorphized in the surface region but could be recrystallized by annealing.

We conclude that also implantation of heavy ions in $LiNbO_3$ can produce waveguides but lattice distortions have to be carefully annealed in order to remove nuclear damage.

The financial support of the Deutsche Forschungsgemeinschaft (SFB 225) is gratefully acknowledged.

A NEW SPI-IONDEP^{TM} PROCESS FOR MODIFICATION OF METALLIC AND CERAMIC SURFACES

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Ion implantation technology offers great potential for treatment of high precision components used in different industrial applications. Surface properties of interest such as wear and corrosion resistance are selectively increased without causing any adverse effects on bulk properties of material. One of the major problems with the ion implantation process is self-sputtering of the surface which seriously limits the final concentration of implanted ions. The problem is more severe when high-Z metallic ions are used.

Spire Corporation has devised the SPI-IONDEP^{TM} process for resolving the sputter limitation during the ion implantation process. In this innovative approach, the geometry during the ion implantation process is arranged such that the sputtered ions from the surrounding media (fixture) will be deposited on the part concurrent with the ion bombardment.

Solid lubricants such as Pb and Ag have been deposited by the process with good uniformity. These coatings are free of pinholes, dense and extremely adherent to the substrate due to the graded interface. The process is equally capable of depositing coatings of refractory metals and should find many uses in the treatment of ceramic surfaces.

The geometry for the patented SPI-IONDEP^{TM} process is described and preliminary results from tests and evaluations will be presented.

ION-BEAM ASSISTED DEPOSITION OF THIN FILMS AND COATINGS

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The bombardment of a thin film with energetic ions during deposition from the vapor phase has been found to produce dramatic changes in the microstructure and related properties of the film. Bombardment has been found to increase the density of films deposited under low adatom diffusion conditions, modify the nucleation and early stages of growth, modify the rate of film coalescence, disrupt columnar grain growth, produce a preferred orientation in the film and improve adhesion of the films. Film stoichiometry can also be controlled by selective implantation of constituent species or by control of the partial pressure of a reactive constituent.

The talk will review important observations from the literature and will include examples from research performed at the author's laboratory. The basis for physical changes in the microstructure will be examined. The lecture will conclude with examples of the application of IAD to the deposition of coatings for tribological, environmental protection and optical applications.

ION-BEAM INDUCED DIAMOND-LIKE CARBON COATINGS

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Diamond-like coatings prepared with the different techniques have many beneficial properties: high hardness, good wear and acid resistance, low friction and high heat conductivity, etc. The special properties of the coatings prepared with ion-beam techniques are good adhesion to the sample surface and low deposition temperature. Additional advantages are achieved by mass-separated ion beams; the coatings have been prepared under very accurate circumstances and they are extremely pure, even isotopically. A general disadvantage in the use of ion beams is the lack of efficient ion sources with which pure carbon layers in long high-beam runs could be produced. One promising and technically rather simple carbon ion source candidate for this purpose is based on pulsed or continuous electric discharge arcs between carbon cathode and anode. By using magnetic fields, the generated plasma beams can be focused, accelerated and curved, which means that the direct preparation of diamond-like coatings is possible. The disadvantage of the system is that the determination of the optimum combination of the parameters is difficult.

ION BEAM MODIFICATION AND ANALYSIS OF HIGH T_c CERAMIC SUPERCONDUCTORS

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The utility of ion beams in the formation, modification, and analysis of thin film high temperature ceramic superconductors has become increasingly obvious over the past year. Recent studies have shown that the new ceramic superconductor can be disordered and amorphized by particle irradiation. Ion implantation has been used to both turn off superconductivity through radiation damage and turn an insulating surface layer into a superconductor by implantation alloying. Ion beam analytical techniques, such as high energy backscattering and nuclear reaction analysis, have been effectively employed in the composition analysis of these new materials. The rapidly developing research results in these areas will be reviewed and discussed.